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A hunt for elusive trace gases in the marine boundary layer

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Abstract

We present a feasibility study into the use of solar remote sensing Fourier transform infrared spectrometry (FTS) to detect elusive trace gases in the marine boundary layer. The study acquired spectra from Wollongong, Australia (34.5°S, 150°E, 30m above sea level) at dawn as the sun rose over the ocean. We hoped to detect elusive atmospheric trace gases such as hypochlorous acid (HOCl) and dinitrogen pentoxide (N₂O₅) in these spectra, since the geometry results in path-lengths through the marine boundary layer in excess of 100km at dawn. Spectra were successfully collected at SZA greater than 90° above the marine horizon on four days due to the effects of diffraction in the atmosphere. Enhanced absorption features were observed for a large number of species and a spectral region for the possible observation of hypochlorous acid was identified. The experimental setup allowed for transmission of some infrared radiation but not enough to generate a sufficient signal to noise ratio for meaningful retrievals of total column amounts. Almost all absorption features were either saturated or had low signal to noise. Despite these problems, FTS has potential and some simple changes to the experimental setup could prove this to be a useful method.

Keywords

trace, gases, hunt, marine, elusive, boundary, layer

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A hunt for elusive trace gases in the marine boundary layer

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Abstract

We present a feasibility study into the use of solar remote sensing Fourier transform infrared spectrometry (FTS) to detect elusive trace gases in the marine boundary layer. The study acquired spectra from Wollongong, Australia (34.5°S, 150°E, 30m above sea level) at dawn as the sun rose over the ocean. We hoped to detect elusive atmospheric trace gases such as hypochlorous acid (HOCl) and dinitrogen pentaoxide (N₂O₅) in these spectra, since the geometry results in path-lengths through the marine boundary layer in excess of 100km at dawn. Spectra were successfully collected at SZA greater than 90° above the marine horizon on four days due to the effects of diffraction in the atmosphere. Enhanced absorption features were observed for a large number of species and a spectral region for the possible observation of hypochlorous acid was identified. The experimental setup allowed for transmission of some infrared radiation but not enough to generate a sufficient signal to noise ratio for meaningful retrievals of total column amounts. Almost all absorption features were either saturated or had low signal to noise. Despite these problems, FTS has potential and some simple changes to the experimental setup could prove this to be a useful method.

Introduction

The marine boundary layer is defined as the part of the atmosphere which is directly affected by physical action at the ocean/ atmosphere interface within one hour. Bubbles breaking the ocean surface and white-capping release aerosols and water vapour into the marine boundary layer. Dissolved gas released from the ocean and entrainment of various species from the free troposphere and continental boundary layer provide the ingredients and conditions for some very important heterogeneous chemical processes.

Measurements in the “clean” marine boundary layer are difficult due to the very low concentrations of the many gases of interest. A large range of methods have been employed to measure different trace gases in the marine boundary but the atmospheric chemistry of the marine boundary layer remains poorly understood because many of the trace gases of interest exist at very low concentrations and are difficult to measure.

Remote sensing of atmospheric trace gases by ground-based solar FTIR spectroscopy presents an intriguing possibility to detect such missing species. The use of spectra recorded at dawn (or dusk) with the sun rising (or setting) over the ocean provides very large path-lengths through the marine boundary layer and thereby increases the sensitivity of the measurements to many species with low concentrations.

Possible target species of interest to marine boundary layer chemistry that have infrared signatures but are yet to be detected in the atmosphere are HOCl, N₂O₅, and ClNO₂. Additionally, earlier remote sensing FTIR measurements from Wollongong have suggested a possible ocean source of OCS [Griffith *et al.*, 1998], so measurements made through the marine boundary layer might provide further evidence for this. This technical report explains the FTS process, potential problems with the technique and future improvements that could be made.

Remote sensing by ground-based solar FTIR spectroscopy at Wollongong

The Fourier Transform InfraRed spectrometer (FTS) located at the University of Wollongong (34.4°S, 150.9°E, 30m above sea level) is a commercial instrument (Bruker HR125) configured for solar remote-sensing measurements. It has an optical setup that comprises a solar tracker on the roof which directs the solar beam into the instrument situated in the laboratory below (see Figure 1).

In these experiments the focus is predominantly on tropospheric gases where pressure broadening of spectral features dominates. Thus a resolution of the order of 0.01 cm⁻¹ is necessary and so a maximum optical path difference of 100 cm was used. A series of narrow optical band-pass filters is employed to reduce noise outside the spectral area of interest and thereby increase the signal-to-noise in the wavenumber region that the gases of interest absorb. The wavenumber ranges of the optical filters used are:

$F1 = 3800\text{-}4600\text{ cm}^{-1}$; $F2 = 2600\text{-}3600\text{ cm}^{-1}$; $F3 = 2200\text{-}3500\text{ cm}^{-1}$; $F4 = 1900\text{-}2900\text{ cm}^{-1}$; $F5 = 1800\text{-}2300\text{ cm}^{-1}$; $F7 = 800\text{-}1500\text{ cm}^{-1}$ & $F8 = 600\text{-}1200\text{ cm}^{-1}$.

A mercury cadmium telluride (*MCT*, HgCdTe) detector is employed in recording spectra from filter regions 7 and 8, and an indium antimonide (InSb) detector used for Filters 1 to 5. InSb and MCT detectors are maintained at 77 K by liquid nitrogen. The entire instrument is maintained at a pressure below 1 hPa.

The analysis of spectra recorded by the FTS requires the calculation of synthetic spectra using a “forward model” of the atmosphere and of the instrument. The atmosphere is divided into a number of different layers and each layer is assigned a temperature, pressure and an initial guess for the mixing ratio of all atmospheric gases that have a spectral signature in the region being analysed.

Total column amounts (molecules per square centimetre in a column from the ground to the top of the atmosphere) of atmospheric gases are retrieved by adjusting the mixing ratio profile until the spectral features of the synthetic spectrum best match those in the measured spectrum [*Pougatchev et al.*, 1995].

Potential problems collecting dawn spectra using FTS

A number of significant challenges need to be overcome for the successful collection of atmospheric absorption spectra at dawn. The first problem was to calculate when sunrise would be visible over the horizon. At the University of Wollongong, this is only possible on a few days each year due to the view of the horizon being obstructed by buildings and large trees.

Second, the extended atmospheric path-length of the experiment at dawn leads to a decrease in the solar radiation reaching the detector. This has an obvious effect on the signal to noise ratio of the experiment. In an attempt to increase the signal to noise ratio the aperture was set to 2mm, a large increase from the usual 0.8mm used in daytime measurements (at higher resolution). As the Sun rises higher in the sky the aperture needs to be stopped down to prevent saturation of the detector and so the spectra with lower SZAs were recorded with smaller apertures. Third, the enhancement of features in the early morning spectra occurs for all absorbing species, and many regions of the spectra are thus absorption saturated.

Fourth, rapidly changing air masses are a major issue. As the Earth rotates, the path-length of radiation from the Sun through the atmosphere to the FTS on the ground changes. The rate of change is at a maximum at dawn and dusk and at a minimum at noon, with the atmospheric path-length decreasing accordingly. To minimise the effect of airmass change we recorded spectra with the fastest scan speed for the moving mirror producing 10 second intervals between spectra.

The fifth problem was optimising the solar tracker settings to ensure the FTS was focussed on the centre of the solar disk. Otherwise distortion and poor definition of the spectrum can result. The solar tracker used for FTS measurements can operate in two modes of tracking. In normal solar tracking mode the tracker is directed to the calculated position of the Sun in the sky and then a quadrant detector is utilised to actively track the Sun to ensure that the solar disc is centred onto the entrance aperture of the spectrometer. The active tracking is only employed when solar intensity is above a set threshold. When the solar intensity is below this threshold then the tracker is simply directed at the calculated position of the sun, with no further adjustment. This mode is called passive tracking, and is not as accurate.

Examples of Successfully collected spectra

Spectra were successfully recorded with very high SZA at dawn from the University of Wollongong, in September and October 2009 and again in March 2010. During these campaigns spectra were recorded above 88° on 11 separate days (see Figure 2 for examples from different filter regions).

The Search for Target Species in Marine boundary layer Spectra

This work examines the possibility of detecting very low concentrations of gases within the marine boundary layer due to the enhancement of absorption features resulting from the very long path-lengths at dawn. Of particular interest here are the species, N_2O_5 , HOCl and OCS. N_2O_5 is a night time NO_x reservoir and, along with HOCl, is considered important in the night time generation of atomic chlorine, which in turn effects the oxidising capacity of the atmosphere, [Pechtl and von Glasow, 2007], [Thornton et al., 2010]. OCS is the major atmospheric sulfur reservoir and the

marine boundary layer is suspected of playing an important role both as sink and a major source for this important gas, [Xu *et al.*, 2001].

Dinitrogen pentoxide (N₂O₅)

The absorption features for N₂O₅ coincide with parts of the spectrum that are already saturated due to the absorptions of other gases. Consequently this technique has no sensitivity to N₂O₅ given the measurement conditions.

Hypochlorous acid (HOCl)

The situation is better for HOCl as the spectral region where HOCl is infrared active is not blacked out in the early morning spectra (see Figure 3). However the HOCl features are not visible in the recorded spectra. The failure of this method to detect HOCl in the atmosphere is not evidence that it is not present in the marine boundary layer. Instead the combination of the small absorption features expected and the low signal-to-noise achieved in the dawn spectra mean that HOCl is below the detection limit for the method. Both the overall signal-to-noise of the spectrum (at the 100% level) and the depth of the absorption feature contribute to the detection limit and so any improvement to the overall signal-to-noise of the spectra will reduce the detection limit. The simulation shown in Figure 3 gives a maximum absorption depth of approximately 0.1% for a simulated boundary layer mixing ratio of 0.4 parts per trillion. Since the overall signal-to-noise of the spectrum in the region of interest is only approximately 20, HOCl is clearly below the detection limit. However because the spectra are not saturated across the spectral region of interest with a modification to the technique a measurement of HOCl may become possible. One obvious improvement to the sensitivity that could be made is to use a much narrower optical bandpass filter to improve the signal-to-noise in the spectra. Assuming that a 1% absorption might be detectable if the signal-to-noise ratio could be improved to better than 100 than a detection limit of 4 parts per trillion might be achievable. It is possible that such a technique might yield an atmospheric detection of HOCl.

Carbonyl Sulfide (OCS)

OCS total column amounts are routinely derived from remote sensing FTS spectra taken at lower SZA. It was hoped that spectra recorded at very high SZA would yield information about OCS in the marine boundary layer. Indeed calculations of the information provided by several synthetically simulated OCS spectra recorded at multiple angles (with a theoretical signal to noise of 100 at 2052.71cm^{-1}) suggested that a fully independent partial column from 0-1 km altitude could be derived. Unfortunately the actual signal to noise achieved was only 20. The large uncertainties that resulted made any sensitivity to boundary layer OCS unattainable using the current experimental setup. It may be possible however to improve the signal to noise ratio in high SZA spectra by the use of an infrared filter with a much narrower bandwidth than currently utilised. It may also be possible to increase the signal to noise by taking longer to record spectra.

Summary and conclusions

Very high SZA spectra ($\text{SZA} > 88^\circ$) were successfully recorded with the sun rising over the ocean at the University of Wollongong on 11 separate days. Some example high SZA spectra were obtained for each of the 7 different optical bandpass filters used. Many of the spectral regions of interest for target trace gas species were saturated in the high SZA spectra making retrievals of gases such as N_2O_5 nearly impossible.

The spectral region where HOCl absorbs is not saturated in the example spectra from Wollongong but there was no evidence of absorption features of HOCl in the spectra. It is thus possible that remote sensing FTS might be a suitable technique for use in the hunt for atmospheric HOCl if the signal-to-noise could be improved e.g. by use of a narrow optical bandpass filter.

Retrievals of OCS have so far resulted in large uncertainties and attempts to get a stable retrieval for a partial column in the marine boundary have so far failed. Any mechanism which improves the signal-to-noise of the spectra may lead to more stable retrievals being obtained.

Despite the lack of success in this initial study, we believe the technique shows some promise and there are mechanisms available that might increase the signal to noise to a workable level. Further work at Wollongong has been halted for the foreseeable future by new buildings which obscure the view to the horizon. Use of narrower optical band filters for the collection of the dawn spectra is recommended in a bid to increase the signal to noise ratio required for meaningful observations of the marine boundary layer to be made.

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Figure Captions

Figure 1: Photographic illustration of the current spectrometer (Bruker model HR125) and solar tracker operated at the University of Wollongong (34.4°S, 150.9°E, 30m above sea level)

Figure 2 Examples of early morning spectra for the seven different filter regions. F3 in black (& offset) has been scaled down by a factor of 4 for easier comparison.

Figure 3 A high SZA spectrum (blue) is compared to a HOCl simulated spectrum (red). Both spectra have been magnified and are not to scale. A number of spectral regions where HOCl absorbs and solar transmission occurs (in the simulated spectra) are clearly visible in this plot.







